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TITLE (54): Method for Continuous Preparation of  
Heterogeneous Ion Exchange Membrane

ABSTRACT (57):

An invention of a method for continuous preparation of a heterogeneous ion exchange membrane. In this invention, a linear low-density polyethylene alloy is used for a binder material of an ion exchange resin, it is continuously formed into a membrane using a four-roller mill, a network is continuously pressed by a network pressing device, and the finished product is continuously taken up by a wind-up roll. The smoothness of the product is excellent, the allowable tolerance of the membrane thickness is less than  $\pm 0.02$  mm, the utilization rate of the raw material is as high as 95% or higher, the production efficiency is twice as high as batch methods or higher, the ion selectivity of the membrane is greater than 90%, and the chemical performance and electrochemical performance of the membrane are uniform.

## Patent Claims

1. A method for preparation of a heterogeneous ion exchange membrane including mixing together a powdery ion exchange resin and a polyolefin binder material, membrane forming, network pressing, and taking up, characterized in that a linear low-density polyethylene alloy is used for a binder material, a membrane is continuously formed using a four-roller mill, a network is continuously pressed by a network pressing device, and the finished product is continuously taken up by a wind-up roller.

2. A method for preparation of a heterogeneous ion exchange membrane as defined in Claim 1, characterized in that the composition of the linear low-density polyethylene alloy includes: 30-50% linear low-density polyethylene (LLDPE), 30-50% ethylene-vinyl acetate (EVA) copolymer, and 20-40% polyisobutylene (PIB).

3. A method for preparation of a heterogeneous ion exchange membrane as defined in Claim 1, characterized in that the operating temperature range of the four-roller mill is 80-150°C, and the rotation speed is 3-10 meters/minute.

4. A method for preparation of a heterogeneous ion exchange membrane as defined in Claim 1, characterized in that a high-temperature instantaneous continuous network pressing technique is used for network pressing, the network fabric is pressed into a membrane utilizing the pressure between the roller drums and the melted condition of the membrane surface, and the temperature range of network pressing is 130-180°C.

5. A method for preparation of a heterogeneous ion exchange membrane as defined in Claim 1, characterized in that the wind-up roller, cooling roller, network fabric guide roller, doubling roller, and carrier roller are operated continuously and synchronously with the four-roller mill and the network pressing device.

## Specification

### Method for Continuous Preparation of Heterogeneous Ion Exchange Membrane

The present invention relates to the invention of a method for continuous preparation of a heterogeneous ion exchange membrane.

Heterogeneous ion exchange membranes are produced in the greatest quantities in China today among functional separation films, and compared with homogenous ion exchange membranes, they have such features as great density, high mechanical strength, and good usability. Following expansion of the scope of application, the quantity of products produced is constantly being renewed; the quantity sold in the international market has doubled in five years, and the quantity sold domestically has tripled in the same period. Today the demands for quality and quantity of the membranes in water treatment engineering such as electrodialysis and corollary equipment are becoming greater and greater. However, in Japanese Unexamined Patent S54-5888 being the prior

art of the day, a polyolefin resin and a powdery anionic exchange resin are mixed using a roller drum or extruder and they are subsequently formed into a membranous material. Said method, in order not to have the electrical resistivity of the membrane rise greatly, and to obtain a heterogeneous ion exchange membrane having high ion mobility and comparatively good mechanical strength, the membrane must be subjected to treatment using hot water at 75°C or higher so as to make the membrane produce partial microcracking, and after that the membrane must be further processed using a polymer or monomer having an ion exchange group that can crosslink with the microcrack portion of the membrane and the surface of the membrane, and the entire technique is performed noncontinuously.

The aim of the present invention is to provide a method for continuous preparation of a heterogeneous ion exchange film. In this invention, a membrane is continuously formed using a four-roller mill, a network is continuously pressed by a network pressing device, and the finished product is continuously taken up by a wind-up roller. The present invention has overcome the drawbacks of the prior art, and in comparison, it has raised the smoothness of the membrane, the utilization rate of the raw material, and the production efficiency.

The present invention uses a mixture of linear low-density polyethylene base alloy (also called low-pressure low-density polyethylene) and powdery ion exchange resin, a four-roller mill to continuously form the membrane, a network pressing device to continuously press the network, and a wind-up roller to continuously take up the finished product. As a result, it provides a method for continuous preparation of a heterogeneous ion exchange membrane.

The composition of the linear low-density polyethylene alloy in the present invention contains 30-50% linear low-density polyethylene (LLDPE), 30-50% ethylene-vinyl acetate copolymer (EVA), and 20-40% polyisobutylene (PIB).

The present invention uses a four-roller mill to continuously form a membrane, and said four-roller mill is made from a rebuilt SY4F1120A.

The diameter of its roller drums is 360 mm, the length of the roller drums is 1120 mm, the rotation speed is 3-10 m/min, and the operating temperature range is 80-150°C.

The present invention uses a high-temperature instantaneous continuous network pressing technique for network pressing, the network fabric is pressed into the membrane sheet utilizing the pressure between the roller drums and the melted condition of the surface of the membrane sheet, and the temperature range of network pressing is 130-180°C.

The present invention continuously prepares heterogeneous ion exchange membranes, the entire unit is in a synchronous operating mode, wherein the wind-up roller, cooling roller, network fabric guide roller, doubling roller, and carrier roller

operate continuously and synchronously with the four-roller mill and the network pressing device.

Of heterogeneous ion exchange membranes prepared using the continuous method, the smoothness of the membrane is excellent, the allowable tolerance of thickness of the membrane in the lateral and longitudinal directions is less than  $\pm 0.02$  mm, the utilization rate of the raw material reaches 95% or higher, the production efficiency is as high as two times or higher compared with the batch method, the ion selectivity of the membrane is greater than 90%, and the chemical performance and electrochemical performance of the membrane are uniform.

The attached drawing is a process flow diagram of continuous sheet formation and continuous network pressing of heterogeneous ion exchange membranes.

The symbols in the drawing are: 1, 2, 3, 4 as four-roller mill, 5, 6, 7, 8 as cooling rollers, 9, 10 as network fabric, 11, 12 as network fabric guide rollers, 13, 14 as network pressing device, 15, 16 as doubling rollers, 17 as wind-up roller, and 18, 19, 20, 21, 22 as carrier rollers.

The transport process of the material following the drawing is: the plasticized base material being rich in ion exchange resin powder is continuously added onto rollers 1 and 2 of four-roller mill, it passes roller 1, roller 2, roller 3, and roller 4, and is milled into membrane sheets meeting the requirements. Two layers of network fabric above and below for reinforcing the ion membrane are used and are led out respectively from network fabric guide rollers 12 and 11 and drawn onto the top and bottom faces of the ion membrane. The two layers of network fabric above and below are pressed into the membrane by network pressing device 13 and 14, after that they pass through cooling rollers 5, 6, 7, 8 and are cooled, and after being continuously cut by a cutting device, the product is wound up by wind-up roller 17. After the product undergoes quality inspection and approval, it is trimmed to dimensions according to the user's requirements, and it is packaged and shipped. The advantages of the present invention can be better understood by referring to the embodiment presented below.

#### Embodiment 1

LLDPE base alloy (composition: 30-50% LLDPE, 30-50% EVA and 20-40% PIB) and powdery ion exchange resin are mixed together at a weight ratio of 1:4 to 1:2 in an open-type two-roller mixer for 5-15 minutes at 120-160°C to be made into a membrane base, the membrane base is transported onto roller 1 and roller 2 of four-roller mill, and it passes through roller 1, roller 2, roller 3, and roller 4 to be milled into a membrane sheet meeting the requirements. Here, the operating temperature of the four-roller mill is 80-150°C. Next, the membrane base together with the top layer network fabric led out from guide roller 12 and the bottom layer network fabric led out from guide roller 11 are simultaneously sent to the network pressing device constituted by roller 13 and roller 14, and the network fabrics are continually pressed into the membrane body

under the conditions of 130-180°C temperature. After that, they are cooled by cooling rollers 5, 6, 7, 8, and after being continuously cut by a cutting device, the product is wound up by wind-up roller 17, and after passing quality inspection and approval, it is trimmed to dimensions according to the user's requirements, and it is wrapped and shipped. The quality of the product is shown in Table 1.

Table 1 Performance of Heterogeneous Ion Exchange Membrane by Continuous Method

Item	Unit	Value
Selectivity	%	91.1
Surface Resistivity	$\Omega/\text{cm}^2$	4.2
Water Content	%	44.9
Exchange Capacity	meq/g (dry)	2.48
Bursting Strength	MPa	0.31
Thickness Tolerance	mm	$\pm 0.02$
Color		light yellow

#### Comparison to Embodiment 1

In addition to using the same ratio of ingredients and mixing conditions as in Embodiment 1, the well-mixed membrane base is cooled to room temperature and then put into a two-roller mixer to be stretched and relaxed. Next, the stretched and relaxed membrane base is put into the mixer to be milled into a membrane at a temperature of 80-100°C, after which it is cut open with a knife and manually removed. A stainless steel template is placed on the removed membrane surface to proceed with manual cutting, and after straightening out, network fabrics are placed on both sides above and below membrane, and polished stainless steel is placed on top. After that, it is sent into a press, pressure is applied at 4-8 MPa, the temperature is raised to 130-150°C, and the temperature is maintained for one hour, then it is cooled and depressurized and the product is removed. The quality of the product is the same as that of Embodiment 1 except that the smoothness is  $\pm 0.04$  mm.

Drawing Attached to Specification